NOTES

A Macroscopic Helix Formation Induced by the Shrinking of a Cylindrical Polymeric Hydrogel

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Since the work of Tanaka *et al.*,[1,2] volume phase transitions of polymeric hydrogels has been a topic intensively studied. Pattern formation in a hydrogel associated with this transition is also of interest,[3—8] since studies on the underlying pattern formation may elucidate mechanical properties of gels and pattern evolutions in some biological systems.

Quasi-hexagonal patterns were found in swelling of an ionized polyacrylamide gel slab by Tanaka *et al.*[3] Afterwards, bubble, bamboo, and tube like patterns were observed in the shrinking of a gel cylinder suddenly immersed into an acetone-rich solution.[4] Similar patterns were observed in poly(*N*-isopropylacrylamide) (PNIPAM) gel induced by temperature,[9] in polyacrylate gel induced by a small molecular agent, dodecylpyridinium chloride (DPC)[10] and in many other cases. Some complicated phenomena as intermediate states in a sudden volume change have also been reported such as whitening of PNIPAM gel at the early stage of gel shinking.[11] In our study, a novel pattern tentatively named "gel helix" was observed during a sudden pH-induced shrinkage of a poly(sodium acrylate/acrylamide) gel cylinder. This process is described qualitatively in this report.

EXPERIMENTAL

The gel was synthesized by a traditional free radial polymerization. 1.53 g of purified acrylic acid, 1.52 g of acrylamide and 83.3 mg of purified *N*,*N*′(methylene bisacrylamide) were dissolved in 10 mL distilled water. After adding 25.7 mg of purified ammonium persulfate, glass capillaries with an inner diameter between 0.2 mm and 0.5 mm were dipped into the solution. The polymerization and crosslinking were carried out for 1 h at 40°C followed by 4 h at 60°C. The poly(acrylic acid/acrylamide) gel cylinders were obtained by gently removing them from the glass capillaries. The gels were then immersed in water overnight to remove residue monomers. After the sample was neutralized by dipping in 0.01 M NaOH aqueous solution for 1 h, gel shrinking was induced by sudden immersion into 0.01 M HCl aqueous solution. The sample was observed in a Leitz optical microscope equipped with a self-built CCD camera. The continuous gel shrinking or swelling process was recorded in real time by a video camera. To enhance contrast of the transparent entity, gels were stained with a small amount of methylene blue.

RESULTS AND DISCUSSION

Both solvent content and pH can induce volume phase transition in polyionic hydrogel. As a contrast to the above experiment, we observed the pattern formation of poly(sodium acrylate/acrylamide) in acetone, following the procedure of Matsuo and Tanaka.[4] The pattern obtained was similar to the earlier observations. However, in the pH-induced volume phase transition, a helical pattern was found as presented in Figure 1. As far as we know, such a gel pattern has not been previously reported.

According to our careful experimental observations (Figure 2), the gel helix or gel spring was formed by the helical movement of a crack on the surface. The shrinking process within our observation time can be roughly divided into three stages: 1) the appearance of a gel helix by the generation of a crack followed by the helical growth of the crack front (Figure 2a to 2d); 2) the global gel twisting and elongation. As a consequence, the viewing fields varied from Figure 2d to 2e; 3) the contraction of the helix period (Figure 2e to 2f) and of

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the global gel. Overall gel shrinking mainly takes place in the final stage while the helix is generated in the first stage.

The gel helix can be right-handed (Figure 1) or left-handed (Figure 2). Although the helical period is sample-dependent to some extent, it seems to be of the same order of magnitude as the cylinder diameter. The length scale of the helix period (between $10^{-1} - 10^{0}$ mm), the time scale of the gel helix formation ($10^{0} - 10^{2}$ s) are quite suitable for experimental studies. In our experiment, the gel cylinder lay on the surface of a glass plate. Within each period in helix formation, the crack front moves relatively slowly on the surface facing the glass plate while much faster in the other "free" half spatial period. The gel helix could not be reproduced,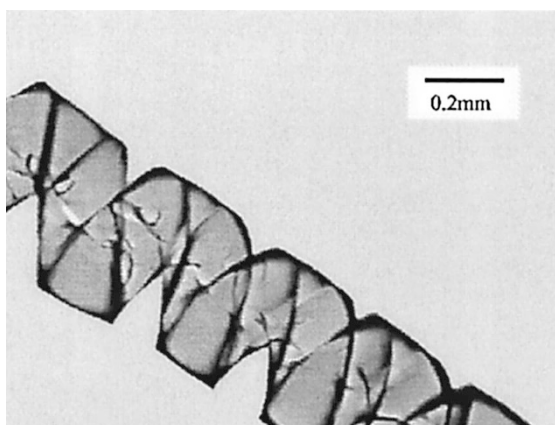 if the acidification of the gel was carried out stepwise. It is interesting that in some experiments even with a sudden acidification, we failed to observe any pattern at first, gel helix formation could nevertheless be triggered by some perturbance such as gentle stretching by tweezers.

It may be emphasized that such a helix formed during a sudden gel collapse cannot be eliminated by re-swelling of gel. Figure 3 demonstrates the re-swelling of a gel after a gel helix had been generated. (In the case of Figure 3a, the gel helix is compressed so tightly that the helical trajectory cannot be resolved, considering that the contrast of the gel is quite low.) The net result from a re-swelling experiment is that helical period is enlarged along with volume change of gel (compare, for instance, Figures 3a and 3f). The original gel cylinder without a crack (before formation of gel helix) could not be recovered at all. A permanent alteration must have happened during the helix formation and thus some chemical crosslinks might be ruptured due to the crack generation in sudden shrinking. The swelling process is, nevertheless, quite complicated with, for instance, a corn-like pattern (Figures 3b and 3c) suggesting a grain coarsening phenomenon. Some intermediate-state patterns such as the worm-like ones (Figures 3d and 3e) are indeed very similar to those of some "transparent animals".[12] Since gels in our experiments are free, the grains disappear eventually, which is similar to the previous observations of gel swelling.[3, 6]

Sekimoto et al.[13, 14] investigated the growth of crack fronts in polymer gels experimentally. They also

Figure 1. A typical gel helix formed in pH-induced gel shrinking.

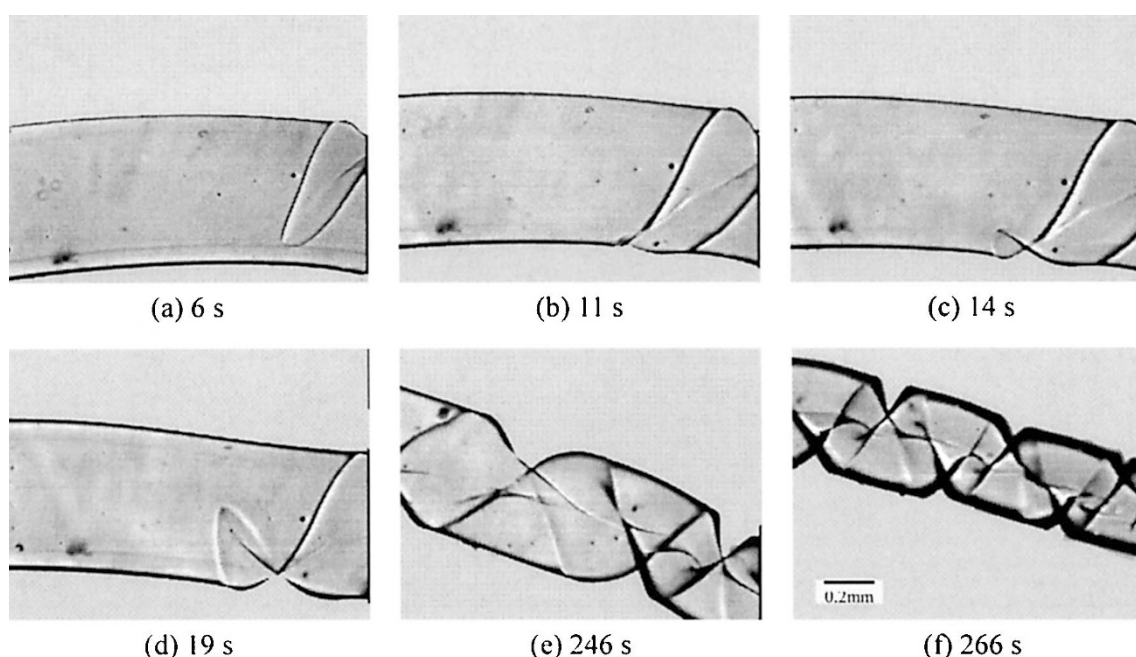(a) 6 s (b) 11 s (c) 14 s

(d) 19 s (e) 246 s (f) 266 s

Figure 2. Real time shrinking process of poly(sodium acrylate/acrylamide) gel cylinder after being dipped into an acid solution with indicated evolution time.
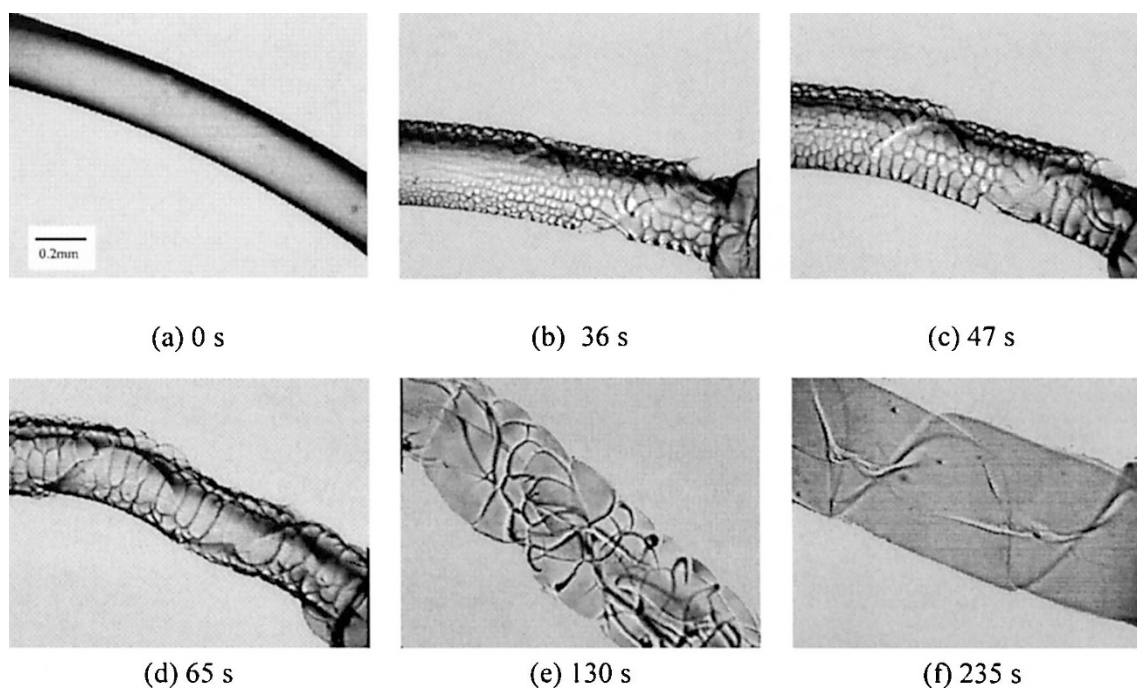
Figure 3. Real time re-swelling process of gel helix after being dipped into a basic solution again (0.01 M NaOH) with indicated evolution time.

pointed out the uniqueness of gel cracks in contrast to those in other materials. But the cracks were artificially generated by two moving slides attached to the gel in their experiments and thus different from those in our gel helix. Several theories have been advanced to deal with pattern formation during gel swelling.[15−19] However, the gel helix is formed in gel shrinking and originates from crack generation. It is unknown whether the present theories can be applied to this problem. Matsuo and Tanaka[4] proposed a qualitative interpretation of gel shrinking. According to their view, a dense skin due to sudden shrinking is a requisite in pattern formation during gel collapse. Various patterns might be formed by some mechanisms of macroscopic phase separation under a constant-volume condition. Based upon these assumptions, bubble and bamboo patterns in gel shrinking have recently been analyzed by the formalism of the Ginzburg–Landau theory.[20] But, it is still puzzling that the gel in our experiment exhibits a bamboo pattern in acetone while a helix pattern is formed by acidification. Associated quantitative theoretical treatments are thus strongly called for.

REFERENCES

1. T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).
2. T. Tanaka, D. Fillmore, S. T. Sun, I. Nishio, G. Swislow, and A. Shah, *Phys. Rev. Lett.*, **45**, 1636 (1980).
3. T. Tanaka, S. T. Sun, Y. Hirokawa, S. Katayama, J. Kucera, Y. Hirose, and T. Amiya, *Nature*, **325**, 796 (1987).
4. E. S. Matsuo and T. Tanaka, *Nature*, **358**, 482 (1992).
5. Z. Hu, X. Zhang, and Y. Li, *Science*, **269**, 525 (1995).
6. Y. Li, C. Li, and Z. Hu, *J. Chem. Phys.*, **100**, 4637 (1994).
7. Z. Hu, Y. Chen, C. Wang, Y. Zheng, and Y. Li, *Nature*, **393**, 149 (1998).
8. M. Amaike, Y. Senoo, and H. Yamamoto, *Macromol. Rapid Commun.*, **19**, 287 (1998).
9. A. Suzuki, S. Yoshikawa, and G. Bai, *J. Chem. Phys.*, **111**, 360 (1999).
10. S. Sakaki and H. Maeda, *J. Colloid Interface Sci.*, **211**, 204 (1999).
11. C. Hashimoto and H. Ushiki, *Polym. J.*, **32**, 807 (2000).
12. S. Johnsen, *Scientific American*, **282**, 80 (2000).
13. Y. Tanaka, K. Fukao, Y. Miyamoto, H. Nakazawa, and K. Sekimoto, *J. Phys. Soc. Jpn.*, **65**, 2349 (1996).
14. Y. Tanaka, K. Fukao, Y. Miyamoto, and K. Sekimoto, *Europhys. Lett.*, **43**, 664 (1998).
15. A. Onuki, *J. Phys. Soc. Jpn.*, **57**, 703 (1988).
16. K. Sekimoto and K. Kawasaki, *J. Phys. Soc. Jpn.*, **57**, 2594 (1988).
17. T. Hwa and M. Kardar, *Phys. Rev. Lett.*, **61**, 106 (1988).
18. N. Suematsu, K. Sekimoto, and K. Kawasaki, *Phys. Rev. A*, **41**, 5751 (1990).
19. K. Sekimoto, *Physica A*, **249**, 262 (1998).
20. J. I. Maskawa, T. Takeuchi, K. Maki, K. Tsujii, and T. Tanaka, *J. Chem. Phys.*, **110**, 10993 (1999).